

*The Japan Society for Analytical Chemistry*

## Certificate of Analysis

### Certified Reference Material

JSAC 0131

JSAC 0132

JSAC 0133

JSAC 0134

### Lead-free Solder (disk form)

### for Fluorescent X-ray Analysis of Metallic Elements

These certified reference materials (CRMs) consist of tin based solder disks whose concentrations of lead, cadmium, silver and copper were certified.

The CRMs are intended primarily for use in evaluating methods of fluorescent X-ray analysis used in the determination of trace metallic elements in products made of lead-free solder. It will be useful to analyze this CRM comparatively with the analytical samples in case of evaluating validity of analytical results of samples.

Each CRM is solder disk of 30 mm diameter and 2.2 mm thickness held in resin, outside dimension is 40 mm in diameter and 4.0 mm thick. 4 disks in different concentration of Pb, Cd, Ag and Cu are packed in a carton case as a set.

Table 1 Certified concentration

CRM	unit	Elements	Certified value $\pm$ uncertainty*	Interlab. standard deviation (SD)	Number of data applied	Main methods of analyses**
JSAC 0131	mg/kg	Pb	13.9 $\pm$ 0.7	1.3	18	(1),(2),(3),(5)
		Cd	(< 3) ***	—	4	(1),(2),(3),(5)
	mass fraction (%)	Ag	0.488 $\pm$ 0.007	0.013	19	(1),(2),(4),(5)
		Cu	0.102 $\pm$ 0.002	0.004	20	(1),(2),(3)
JSAC 0132	mg/kg	Pb	520.9 $\pm$ 8.9	18.3	19	(1),(2),(3),(5)
		Cd	88.0 $\pm$ 3.2	6.5	19	(1),(2),(3),(5)
	mass fraction (%)	Ag	2.98 $\pm$ 0.02	0.05	17	(1),(2),(4),(5)
		Cu	1.01 $\pm$ 0.02	0.03	20	(1),(2),(3)
JSAC 0133	mg/kg	Pb	1022 $\pm$ 19	38	19	(1),(2),(3),(5)
		Cd	832 $\pm$ 9	20	20	(1),(2),(3),(5)
	mass fraction (%)	Ag	3.41 $\pm$ 0.02	0.04	18	(1),(2),(4),(5)
		Cu	0.756 $\pm$ 0.009	0.020	20	(1),(2),(3)

JSAC 0134	mg/kg	Pb	2007 ± 25	51	19	(1),(2),(3),(5)
		Cd	1530 ± 17	36	20	(1),(2),(3),(5)
	mass fraction (%)	Ag	3.91 ± 0.03	0.07	19	(1),(2),(4),(5)
		Cu	0.513 ± 0.009	0.020	20	(1),(2),(3)

\* Uncertainty was calculated by the following equation:

(Student's  $t \times$  interlab standard deviation)  $\div$  (root of number of data applied)

\*\* Refer the clause "procedure for certification of the concentration" in this document.

\*\*\* less than quantification limit

### Instructions for use

1. On handling the CRM disks, hold the disks at their edges, never touch their top and bottom surfaces.
2. Keep the disks in the carton case immediately after use, and close the case with cover.
3. It is inhibited that the CRMs contact the organic solvents, because the disks will be damaged by organic solvents. Never place disks directly on a poly vinyl chloride sheet or materials that contain plasticizers.
4. In case of comparing the analytical results of CRM disk to those of material to be measured, it is necessary to consider that differences in material, thickness or surface character will affect to X-ray intensity.
5. The CRMs are ideally homogeneous, however they often deviate from this ideal because of sample macroscopic effects and unrepresentative conditions at its surface. More than 10 mm diameter of X-ray beam is preferable in order to avoid above effects
6. Handle the CRM in accordance with the safety regulation on the materials which contain Sn, Ag, Cu, Pb and Cd.

### Storage of CRM and expiration of certification

The CRM should be stored in the carton case at room temperature and no exposure to direct sun light.

Stability monitoring tests are being carried out for these CRMs. The results are reported on the JSAC homepage.

### Preparation of CRM and confirmation of its homogeneity

8.3 kg of metallic grainy tin(Mitsuwa Chemicals Co.,Ltd, purity : more than 99.99 %) for JSAC 0131 and lead-free solder(Ishikawa Metal Co.,Ltd, EBASOL J3, Sn-Ag3.0-Cu0.5) for JSAC 0132, 0133, 0134 were prepared as raw materials respectively. The raw materials(tin/solder) were heated in a melting pot (maximum heating capacity is 550 °C). Weighed necessary amount of metallic elements Ag, Cu, Pb, Cd were added into a molten pool of tin/solder. Molten tin/solder was stirred and metallic elements added were dissolved in molten tin/solder sufficiently. Surface of molten tin/solder was covered by reducing agent in order to prevent oxidation of tin/solder. After cooling in room temperature, the reducing agent was removed from solid tin/solder blocks. Tin/solder blocks were re-melted and poured into stainless steel mold (600

mm length, 215 mm width, 25 mm height). The mold was cooled by water so that tin/solder solidified rapidly in order to have a fine and homogeneous metallic structure. 8 mm thick tin/solder blocks were taken off from the stainless mold and grinded to remove the surface impurities. Tin/solder materials were rolled into 2.4 mm thick plates by cold roll mill. 30 mm diameter disks were cut off by rotating cutter from a plate. 327 disks for JSAC 0131, 303 disks for JSAC 0132, 295 disks for JSAC 0133 and 326 disks for JSAC 0134 were produced respectively. 0.2 mm thickness of top and bottom surfaces of disks are removed by lathe, then disks of 30 mm diameter and 2.0 mm thickness are used for homogeneity and interlaboratory cooperative study. For CRMs, 0.2 mm of top surface was removed and finally solder disks of 30 mm diameter and 2.2 mm thickness were held by resin forming 40mm diameter and 4 mm thickness.

For each level of candidate CRM, 10 disks were extracted for homogeneity test in same intervals from disk cutting off order. Concentrations of Ag, Cu, Pb and Cd were analyzed in duplicate by fluorescent X-ray analysis (beam diameter : 25 mm). Relative combined standard deviations of within-disk-repeatability and between-disks were as follows;

JSAC 0131 ; Ag : 2.7 %, Cu : 2.6 %,

JSAC 0132 ; Ag : 1.6 %, Cu : 2.3 %, Pb : 3.5 %, Cd : 7.3 %

JSAC 0133 ; Ag : 0.6 %, Cu : 0.8 %, Pb : 1.8 %, Cd : 1.6 %

JSAC 0134 ; Ag : 1.1 %, Cu : 2.0 %, Pb : 0.9 %, Cd : 1.7 %

For each candidate JSAC 0133 and JSAC 0134, a disk were selected for within-disk homogeneity test by fluorescent X-ray analysis using smaller beam diameter, 8 mm. Concentrations of Ag, Cu, Pb and Cd were analyzed in duplicate at five points ; center, top-side, left-side, bottom-side, right-side in a disk surface. Relative combined standard deviations of repeatability at a point and between-points were as follows;

JSAC 0133 ; Ag : 0.4 %, Cu : 1.2 %, Pb : 0.8 %, Cd : 3.8 %

JSAC 0134 ; Ag : 1.3 %, Cu : 2.4 %, Pb : 2.5 %, Cd : 4.1 %

### Procedure for certification of the concentration

For each level of candidate CRM, 20 disks were extracted in same intervals from disk cutting off order and distributed to 20 laboratories. Four elements (Ag, Cu, Pb and Cd) in these disks were determined in duplicate by each laboratory and reported. The analytical methods were based on JIS Z 3910 ; 2008 “Methods for chemical analysis of solder”. The certified values were obtained by statistical calculation of the results submitted from laboratories.

#### 1. Analytical methods and elements

- (1) Nitric acid • hydrochloric acid digestion—ICP-AES : Ag, Cu, Pb, Cd
- (2) Nitric acid • hydrofluoric acid digestion—ICP-AES : Ag, Cu, Pb, Cd
- (3) Nitric acid • hydrochloric acid digestion—ICP-MS : Cu, Pb, Cd
- (4) Acid digestion • potassium thiocyanate titrimetry : Ag
- (5) Other methods

## 2. Operation of interlaboratory comparison study

The study was operated in the term, November, 2008 through January, 2009.

## 3. Evaluation of results and their certification

$z$  scores in robust method\*\* for each reported analytical results were calculated, and the values providing absolute value of  $z$  score more than 3 were not accepted for statistical calculation of certification. Then, Average, 95 % confident interval(U95%) and between-laboratory reproducibility standard deviation(SD) were calculated as the usual way\*\*\*. The results are shown in Table 1. Ratio of U95% to assigned value of Cd/JSAC 0131 was over 20%, therefore Cd/JSAC 0131 was regarded as less than quantification limit.

\*\* refer to ISO 5725-5:1998

\*\*\* refer to ISO 5725-2:1994

## Date of certification

June 8, 2009

## Laboratories cooperated for the certification (members of the interlaboratory cooperative study)

SII NanoTechnology Inc.

Kobelco Kaken Co., Ltd.

Shimadzu Techno-research Inc.

Sumika Chemical Analysis Service Ltd.

Nittech Research Corp.

Furukawa Electric Co.,Ltd.

Kankyo Giken Co.

Mitsui Kagaku Analysis Center Co.

Nissan Arc Co.

Toray Research Center Corp.

Toshiba Nanoanalysis Corp.

Joetsu Environmental Science Center

Chemicals Evaluation and Research Institute

Environmental Technology Service Co., Ltd.

Konica Minolta Technology Center

Sumitomo Metal Technology-Wakayama

Tokai-techno Co., Ltd

TOSHIBA Lighting & Technology Corporation

Analysis Center Co., Ltd.

Horiba Ltd. Analytical Center

20 laboratories in total

## Distributor

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## Laboratory of preparation

Environmental Technology Service Co., Ltd. (Kitakyushu, Japan)

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